

[54] **SUBSTITUTED CYCLOPROPANECARBOXYLIC ACID ESTERS AND PESTICIDAL COMPOSITIONS CONTAINING THE SAME AS ACTIVE INGREDIENT**

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[21] Appl. No.: 134,589

[22] Filed: Mar. 27, 1980

[30] **Foreign Application Priority Data**

Mar. 30, 1979 [JP] Japan ..... 54-39021  
Jun. 12, 1979 [JP] Japan ..... 54-74387

[51] Int. Cl.<sup>3</sup> ..... A01N 53/00

[52] U.S. Cl. ..... 424/305; 560/124

[58] Field of Search ..... 560/124; 424/305

[56] **References Cited**

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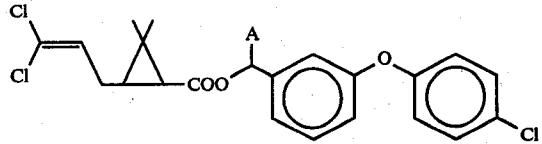
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*Attorney, Agent, or Firm*—Oblon, Fisher, Spivak,  
McClelland & Maier

[57]

**ABSTRACT**

A new pyrethroid compound which is low in toxicity to fish and a pesticidal composition containing the same as an active ingredient are provided. The above pyrethroid compound is a substituted cyclopropanecarboxylic acid ester of the general formula:



(wherein A is a hydrogen atom or an ethynyl group)  
Despite its broad pesticidal spectrum and high pesticidal activity, this ester is very low in toxicity to man and domestic animals and especially low in toxicity to fish as compared with the conventional pyrethroid compounds.

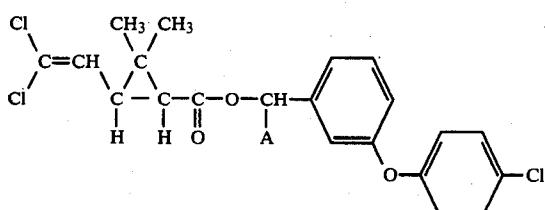
**1 Claim, No Drawings**

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**SUBSTITUTED CYCLOPROPANECARBOXYLIC  
ACID ESTERS AND PESTICIDAL  
COMPOSITIONS CONTAINING THE SAME AS  
ACTIVE INGREDIENT**

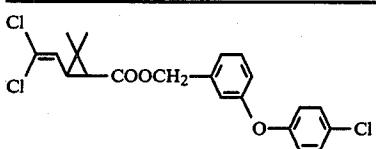
**SUMMARY OF THE INVENTION**

This invention relates to a substituted cyclopropanecarboxylic acid ester of the following general formula (I) and a pesticidal composition containing the same as an active ingredient.

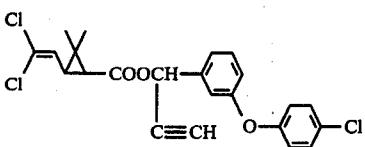


(wherein A is a hydrogen atom or an ethynyl group)

The substituted cyclopropanecarboxylic acid ester of general formula (I) comprises the following two compounds.



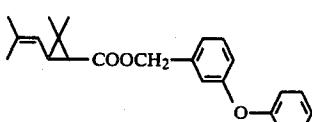
30 3-(4-Chlorophenoxy)benzyl  
2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate  
[hereinafter referred to as Compound (1)]



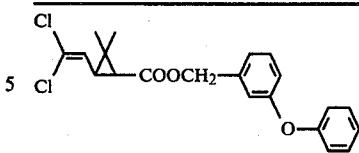
35 40 45 50 55 60 65 3-(4-Chlorophenoxy)-α-ethynylbenzyl  
2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate  
[hereinafter referred to as Compound (2)]

**BACKGROUND OF THE INVENTION**

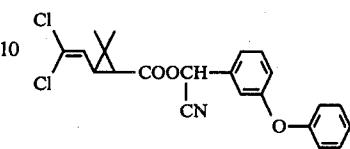
Several improved synthetic pyrethroid pesticides have been developed in recent years and, for example, the following synthetic pyrethroid compounds described in the Proceedings of the Tenth Symposium on Agricultural Chemicals (published Sept. 15, 1977), in particular, are now being evaluated for their practical applicability because they have been found to have the advantages mentioned below.



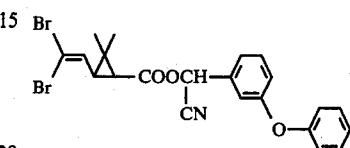
Phenothrin  
[hereinafter referred to as Compound (A)]



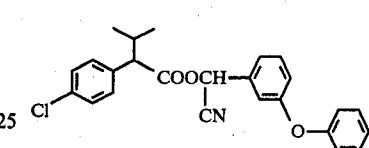
Permethrin  
[hereinafter referred to as Compound (B)]



Cypermethrin  
[hereinafter referred to as Compound (C)]



Decamethrin  
[hereinafter referred to as Compound (D)]



Fenvalerate  
[hereinafter referred to as Compound (E)]

These compounds are characterized by:

- (1) exceptionally high and fast-acting pesticidal effect;
- (2) a minimum of environmental residue which is a problem with organochlorine pesticides, whilst they have sufficiently high residual activity;
- (3) comparatively low toxicity to man and domestic animals; and
- (4) high pesticidal activity even against pests resistant to organophosphorus and/or carbamate pesticides.

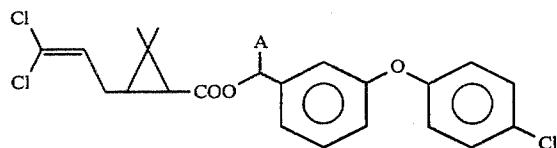
Nonetheless, as pointed out in Kagaku-to-Seibusu (Chemistry and Life) 14, 8 pages 549-556, natural pyrethrin and synthetic pyrethroid pesticides have very high toxicity to fish as compared with the organophosphorus, carbamate or chlorine-type pesticides thus far employed. This means that when such pyrethroid pesticides are applied to a paddy field for the control of agricultural pests, a water area for the control of aquatic pests such as the larvae of mosquitos, sand flies, etc. or a large tract of land including a lake, pond or river, for example by broadcasting from aircraft, these pesticides could destroy the fish inhabiting there. Certain pyrethroid pesticides less toxic to fish were described of late in German Offenlegungsschrift No. 2825197 and it is understood that these compounds represent some improvements in toxicity to fish. However, these pesticides are still by far more toxic to fish than the commonly used organophosphorus, carbamate and chlorine-type pesticides and are not satisfactory for use in the above-mentioned applications.

The intensive study undertaken by the present inventors with a view to developing a safe pesticidal compound which would possess all of the above-mentioned advantages of pyrethroid pesticides, (1) to (4), and, yet, be low in toxicity to fish has revealed that the substituted cyclopropanecarboxylic acid esters of the general formula (I) not only have the above-mentioned advantages (1) to (4) but, to our surprise, have a toxicity to fish which is only 1/5 to 1/1000 of the toxicity of the above pyrethroid pesticides known to have a reduced toxicity to fish and only 1/10 to 1/3000 of the toxicity of

the above-mentioned synthetic pyrethroid compounds [i.e. Compounds (A), (B), (C), (D) and (E)]. It was also found that the substituted cyclopropanecarboxylic acid esters of general formula (I) each have a broadened pesticidal spectrum, displaying an unexpectedly high killing effect even on planthoppers to which many of the conventional pyrethroid pesticides are only very sparingly lethal, and do not cause any injury to crop plants. This invention is the culmination of the above findings.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to new pyrethroid compounds which are substituted cyclopropanecarboxylic acid esters of the general formula:



wherein A is a hydrogen atom or an ethynyl group. The subject compounds possess potent, broad spectrum pesticidal activity and are low in toxicity to man, and domestic animals and particularly low in toxicity to fish.

The pesticidal activity of the compounds according to this invention against green rice leafhoppers (*Nephrotettix cincticeps* Uhler), rice stem borers (*Chilo suppressalis* Walker), tobacco cutworms (*Prodenia litura* Koch) and houseflies (*Musca domestica*), as examples of the pests against which the same compounds are consid-

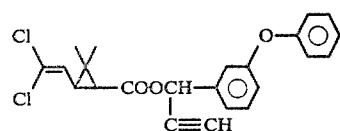
ered effective, the acute toxicity data on the same compounds as determined in rat by the oral route and the median tolerance limit (TLm) data on the same compounds as determined in killifish (*Orizias latipes*) and guppies (*Lebistes reticulatus*) are shown in Table 1 alongside the corresponding values for various control compounds. The pesticidal effects were determined by the procedures set forth in Test Examples 1 through 4, while the acute toxicity to rat was determined by the procedure set forth in Test Example 9 and the toxicity to fish was determined by the procedures set forth in Test Examples 6 and 7, all those Examples appearing hereinafter.

As will be apparent from Table 1, Test Examples 5 and 8, and Utility Examples 1 and 5 which appear hereinafter, Compounds (1) and (2) according to this invention are at least equivalent or superior in pesticidal effectiveness to control compounds (A), (B), (C), (D), (E), (F), (G) and (H) and, yet, are lower in toxicity to fish than the same control compounds, the toxicity values for our compounds being only one-fifth (1/5) to one-three thousandth (1/3000).

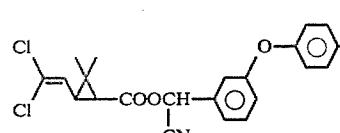
In view of higher pesticidal activity and excellent low toxicity, the Compounds (1) and (2) each consisting principally or essentially of the trans-isomer in relation to the three-membered ring structure are particularly preferable. Compound (2) consisting principally or essentially of the trans-isomer is the most preferable since it is outstanding in pesticidal activity against various pests and is by far low in toxicity to fish, thus being an ideal pesticidal compound which find no equals among pyrethroid compounds which we know of.

TABLE 1

Test compound	Pesticidal Effects					Toxicity to fish	
	Green rice leafhopper ( <i>Nephrotettix cincticeps</i> Uhler) 0.01 µg/Female (%)	Rice stem borer ( <i>Chilo suppressalis</i> Walker) 1.0 µg/Larva (%)	Tobacco cutworm ( <i>Prodenia litura</i> Koch) 0.1 µg/Larga (%)	Housefly ( <i>Musca domestica</i> ) 1.0 µg/Female (%)	Acute oral toxicity to rat LD <sub>50</sub> (mg/kg)	TLm (48 hrs.), ppm Killifish ( <i>Orizias latipes</i> )	Toxicity to fish Guppy ( <i>Lebistes reticulatus</i> )
Compounds of this invention (cis/trans- = 50:50)							
Compound (1)	100	100	100	100	>3000	>10	>5
Compound (2)	100	100	100	100	>3000	>10	>10
Control compounds (cis/trans- = 50:50)							
Compound (A)	80	45	35	100	—	—	—
Compound (B)	80	95	85	100	300	0.040	<0.5
Compound (C)	100	95	100	100	310	0.026	<0.5
Compound (D)	100	100	100	100	—	—	<0.5
Compound (E)	100	100	100	100	440	—	<0.5
	100	—	—	100	—	—	<0.5



[hereinafter, Compound (F)]



[hereinafter, Compound (G)]

TABLE 1-continued

Test compound	Pesticidal Effects						Toxicity to fish TLm (48 hrs.), ppm
	Green rice leafhopper ( <i>Nephrotettix</i> <i>cincticeps</i> Uhler 0.01 µg/Fem- ale (%)	Rice stem borer ( <i>Chilo sup-</i> <i>pressalis</i> Walker 1.0 µg/Larva (%)	Tobacco cutworm ( <i>Prodenia</i> <i>litura</i> Koch 0.1 µg/ Larga (%)	Housefly ( <i>Musca</i> <i>domes-</i> <i>tica</i> 1.0 µg/Fem- ale (%)	Acute oral toxicity to rat LD <sub>50</sub> (mg/kg)	Killifish ( <i>Ori-</i> <i>zias</i> <i>latipes</i> )	Guppy ( <i>Lebistes</i> <i>reticu-</i> <i>latus</i> )
	100	90	60	100	—	—	—

[hereinafter, Compound (H)]

Compounds (1) and (2) according to this invention have excellent pesticidal activity against both the sensitive and resistant strains of pests belonging to the following Orders, displaying a broad pesticidal spectrum. Moreover, the compounds are effective against these pests in all or some of their growth stages.

Order THYSANURA: e.g., *Ctenolepisma villosa* Escherich;

Order COLLEMBOLA: e.g., *Anurida trioculata* Kinoshita, *Onychiurus pseudarmatus* yagii Miyoshi, *Sminthurus viridis* Linne, *Bourletiella hortensis* Fitch;

Order ORTHOPTERA: e.g., Northern cone-headed long horn grasshopper (*Homorocoryphus jezoensis* Matsumura et Shiraki), Vegetable grosshopper (*P. sapporensis* Shiraki), Emma field cricket (*Teleogryllus emma* Ohmachi et Matsura), Doenitz cricket (*Loxoblemmus doenitzii* Stein), Cockroach (*Blattella germanica* Linne), *Gryllotalpa africana* Palisot de Beauvois, *Periplaneta fuliginosa* Serville;

Order ISOPTERA: e.g., *Coptotermes formosanus* Shiraki;

Order MALLOPHAGA: e.g., *Menopon gallinae* Linne, *Damalinia equi* Denny, *Trichodectes canis* De Geer;

Order ANOPLURA: e.g., *Haematopinus eurysternus* Nitzsch;

Order THYSANOPTERA: e.g., Onion thrips (*Thrips tabaci* Lindeman), *Hercinothrips femoralis* Reuter;

Order HEMIPTERA: e.g., White-backed planthopper (*Sogatella furcifera* Horvath), Brown planthopper (*Nilaparvata lugens* Stål), Small brown planthopper (*Laodelphax striatellus* Fallén), Green rice leafhopper (*Nephrotettix cincticeps* Uhler), Zigzag-striped leafhopper (*Inazuma dorsalis* Motschulsky), Black rice bug (*Scotinophara lurida* Burmeister), Rice stink bug (*Lagynotomus elongatus* Dallas), Corbett rice bug (*Leptocorixa corbetti* China), Southern green stink bug (*Nezara viridula* Linne), Grain aphid (*Rhopalosiphum padi* Linne), Japanese grain aphid (*Macrosiphum akebiae* Shinji), Corn leaf aphid (*Rhopalosiphum maidis* Fitch), Green peach aphid (*Myzus persicae* Sulzer), Cotton aphid (*Aphis gossypii* Glover), Foxglove aphid (*Aulacorthum solani* Kalttenbach), Soy bean aphid (*Aphis glycines* Matsumura), Small bean bug (*Chauliops fallax* Scott), Bean bug (*Riptortus clavatus* Thunberg), Common green stink bug (*Nezara antennata* Scott), Unibanded stink bug (*Piezodorus rubrofasciatus* Fabricius), Sloe bug (*Dolycoris baccarum* Linne), Oriental chinch bug (*Cavelerius saccharivorus* Okajima), Sugarcane cottony aphid (*Ceratovacuna lanigera* Zehntner), Cabbage aphid (*Brevicoryne brassicae* Linne), Small green plant bug (*Lygus lucorum* Meyer-

Dur), Onion aphid (*Neotoxoptera formosana* Takahashi), Arrowhead scale (*Unaspis yanonensis* Kuwana), California red scale (*Aonidiella aurantii* Maskell), *Viteus vitifolii* Fitch, Grape leafhopper (*Erythroneura apicalis* Nawa), Grape whitefly (*Aleurolobus taonabae* Kuwana), Ume globose scale (*Eulecanium kunoense* Kuwana), Chrysanthemum aphid (*Macrosiphoniella sanborni* Gillette), Rose aphid (*Macrosiphum ibarae* Matsumura), Azalea lacewing bug (*Stephanitis pyrioides* Scott), Fern scale (*Pinnaspis aspidistrae* Signoret);

Order TRICHOPTERA: e.g., *Oecetis nigropunctata* Ulmer;

Order DIPTERA: e.g., Rice steam maggot (*Chlorops oryzae* Matsumura), Rice leaf miner (*Agromyza oryzae* Munakata), Small rice leaf miner (*Hydrellia griseola* Fallén), Paddy steam maggot (*Hydrellia sasakii* Yuasa et Ishitani), Wheat thigh chloropid fly (*Meromyza salitatrix* Linne), Leaf miner, Wheat blossom midge (*Sitodiplosis mosellana* Gehin), Soy bean root miner (*Melanagromyza dolichostigma* DE Meijere), Soy bean steam midge (*Profetiella soya* Monzen), Soy bean stem miner (*Melanagromyza sojae* Zehntner), Soy bean pod gall midge (*Aspomyia* sp.), Seed maggot (*Hylemya platura* Meigen), Onion maggot (*Hylemya antiqua* Meigen), Stone leek leaf miner (*Phytobia cepae* Hering), Narcissus bulb fly (*Lampetia equestris* Fabricius), House fly (*Musca domestica* vicina), Mosquito (*Culex pipiens*);

Order APHANOPTERA: e.g., *Xenopsylla cheopis* Rothschild, *Pulex irritans* Linne;

Order HYMENOPTERA: e.g., *Dolerus hordei* Rohwer, Soy bean sawfly (*Takeuchiella pentagona* Malaise);

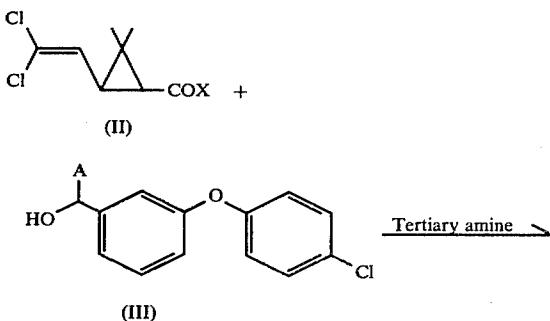
Order LEPIDOPTERA: e.g., Rice stem borer (*Chilo suppressalis* Walker), Yellow rice borer (*Tryporyza incertulas* Walker), Pink borer (*Sesamia inferens* Walker), *Pelopidas mathias* oberthuri Evans, Grass leaf roller (*Cnaphalocrosis medinalis* Guénée), Rice leaf roller (*Susumia exigua* Butler), Rice green caterpillar (*Naranga aenescens* Moore), Armyworm (*Leucania separata* Walker), Corn borer (*Ostrinia survacalis* Guénée), Sweetpotato leaf folder (*Brachmia triannulella* Herrich-Schaaffer), Bindweed leaf miner (*Bedellia sommlentella* Zeller), Sweetpotato leaf worm (*Aedia leucomelas* Linne), Flax budworm (*Heliothis viresplaca* adaucta Butler), Tobacco striped caterpillar (*Pyrrhia umbra* Hufnagel), Bean webworm (*Syphle ruralis* Scopoli), Soy bean pod borer (*Grapholita glyciniivorella* Matsumura), Azuki pod worm (*Matsumuraes phaseoli* Matsumura), Lima-bean pod borer (*Etiellazinckenella* Treitschke), Oriental tobacco

budworm (*Helicoverpa assulta* Guénée), Peppermint pyrausta (*Pyrausta aurata* Scopoli), Peacock butterfly, Lilac pyralid (*Margaronia nigropunctalis* Bremer), Sugarcane shoot borer (*Eucosma schistaceana* Sellen), Cabbage armyworm (*Mamestra brassicae* Linné), Tobacco cutworm (*Plodenia litura* Fabricius), Common cutworm (*Agrotis fucosa* Butler), Common cabbageworm (*Pieris rapae crucivora* Boisduval), Crucifer caterpillar (*Mesographe forficalis* Linné), Diamond-back moth (*Plutella maculipennis* Curtis), Cotton caterpillar (*Margaronia indica* Saunders), Stone leek miner (*Acrolepia alliella* Semenov et Kuznetsov), Citrus leaf miner (*Phyllocnistis citrella* Stainton), Smaller citrus dog (*Papilio xuthus* Linné), Peach fruit moth (*Carposina niponensis* Walsingham), Oriental fruit moth (*Grapholitha molesta* Busck), Summer fruit tortrix (*Adoxophyes orana* Fischer von Roslerstamm), Gypsy moth (*Lymantria dispar* Linne), Tent caterpillar (*Malacosoma neustria testacea* Motschulsky), Small grape plume moth (*Stenoptilia vitis* Sasaki), Persimmon fruit moth (*Stathmopoda flavofasciata* Nagano), Fall webworm (*Hyphantria cunea* Drury), Japanese lawn grass cutworm (*Rusidrina depravata* Butler), *Pectinophora gossypiella*;

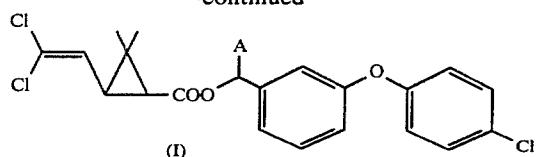
Order COLEOPTERA: e.g., Rice leaf beetle (*Oulema oryzae* Kuwayama), Large 28-spotted lady beetle (*Henosepilachna vigintioctomaculata* Motschulsky), 28-spotted lady beetle (*H. vigintioctopunctata* Fabricius), False melon beetle (*Atrachya menetriesi* Faldermann), Two-striped leaf beetle (*Paraluperodes nigrolineatus* Motschulsky), Bean leaf beetle (*Colpocephalis signata* Motschulsky), Bean frosted weevil (*Eugnathus distinctus* Roelofs), Castaneous garden beetle (*Maladera castanea* Arrow), Soy bean beetle (*Anomala rufocuprea* Motschulsky), Bean blister beetle (*Epicauta gorhami* Marseul), Peppermint leaf beetle (*Chrysolina exanthematica* Wiedemann), Olive engraved weevil (*Hylobius cribripennis* Matsumura et Kono), Vegetable weevil (*Listroderes obliquus* Klug), Cucurbit leaf beetle (*Aulacophora femoralis* Motschulsky), Boll weevil (*Anthonomus grandis* Boh.), Rice weevil (*Sitophilus zeamais* Motschulsky), Lesser grain borer (*Rhizopertha dominica* Fabricius), Azuki bean weevil (*Callosobruchus chinensis* Linné), Mustard beetle (*Phaedon cochleariae* Fab.), Boll weevil;

Order ACARINA: e.g., Winter grain mite (*Penthaleus major* Dugès), Two-spotted spider mite (*Tetranychus urticae* Koch), Carmine mite (*Tetranychus telarius* Linné); and so forth.

The substituted cyclopropanecarboxylic acid esters of general formula (I) can be easily produced, for example by the following method.



-continued



[wherein A has the same meaning as defined in general formula (I); and X is a halogen atom]

Thus, the above process is carried out by reacting a 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbonyl halide of general formula (II) with a substituted benzyl alcohol of general formula (III) in the presence of a tertiary amine such as pyridine, triethylamine or the like.

In putting to use the compounds according to this invention, each of them or a mixture thereof may be employed as it is. However, for the sake of ease of handling, it is generally an acceptable practice to formulate the compounds with suitable carriers or vehicles to prepare stock preparations and, then, dilute them as required. The applicable formulations include, for example, emulsifiable concentrates, wettable powders, dusts, granules, microgranules, oil preparations, aerosols, thermal fumigants (fumigation coils, electric fumigation mats or other formed articles), non-thermal fumigants, baits, etc. These and other optional formulations may be prepared by the established manufacturing procedures for agricultural chemicals and may be selectively applied according to the intended use.

Unlike the conventional chrysanthemummonocarboxylates, the compounds according to this invention are highly stable against light, heat, oxidation, etc. However, if it is considered necessary, for example when exposure to a highly oxidative environment is expected, compositions with stabilized efficacy can be prepared by incorporating suitable amounts of oxidation inhibitors or ultraviolet absorbers such as phenol derivatives, e.g. BHT, BHA, etc., bisphenol derivatives, arylamines such as phenyl- $\alpha$ -naphthylamine, phenyl- $\beta$ -naphthylamine, phenetidine-acetone condensate, etc. or/and benzophenone compounds as stabilizers.

Generally such a pesticidal composition contains 0.01 to 95 weight percent, preferably 0.1 to 90 weight percent, of the compound according to this invention.

The compounds according to this invention can be used in the above-mentioned various formulations and in various application forms obtainable by processing the formulations further to suit the purpose. In such secondary application forms, the content of the compound according to this invention may vary in a very wide range. Thus the concentration of said compound in an application form is 0.0000001 to 100 weight percent, preferably 0.0001 to 10 weight percent.

The pesticidal compositions according to this invention can be applied by the conventional application method or methods suited for each application form.

The following Examples of Synthesis, Test Examples, Formulation Examples and Utility Examples are intended to further illustrate this invention and should by no means be construed as limiting the scope of the invention. In the Formulation Examples, all parts are by weight.

## EXAMPLE OF SYNTHESIS-1

In 20 ml of dry benzene was dissolved 2.28 g of cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbonyl chloride, followed by addition of 2.34 g of 3-(4-chlorophenoxy)benzyl alcohol and 1.58 g of pyridine. The mixture was stirred at room temperature overnight. Thereafter, the reaction mixture was washed with dilute hydrochloric acid and water, dried over anhydrous magnesium sulfate and distilled under reduced pressure to remove a low-boiling fraction, whereby an oily product was obtained as a residue. This oil was purified by preparative liquid chromatography [column: Waters Associates' Prep LC/System 500, Prep PAK ® 500/SILICA; solvent system: diisopropyl ether:n-hexane=6:94, v/v]. The above procedure yielded 3.91 g of 3-(4-chlorophenoxy)benzyl cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbonylate (yield 92%).

The above procedure was repeated except that trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbonyl chloride was used in lieu of cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbonyl chloride. This procedure yielded 3.81 g of 3-(4-chlorophenoxy)benzyl trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbonylate (yield 90%).

The above product compounds have the following NMR spectra.

NMR spectra (90 MHz)  $\delta_{HMS}^{CDCl_3}$ :

cis-Compound: 1.17(s)6H, 1.72-2.08(m)2H, 5.00(s)2H, 6.18(d)1H, 6.80-7.38(m)8H

trans-Compound: 1.11(s)3H, 1.21(s)3H, 1.56(d)1H, 2.18(dd)1H, 5.03(s)2H, 5.53(d)1H, 6.80-7.38(m)8H

## EXAMPLE OF SYNTHESIS-2

In 120 ml of dry benzene was dissolved 11.4 g of 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbonyl chloride (cis-/trans-ratio=50:50, approx.) followed by addition of 12.9 g. of 3-(4-chlorophenoxy)- $\alpha$ -ethynylbenzyl alcohol and further by dropwise addition of 7.9 g of pyridine. The mixture was stirred at room temperature overnight. Thereafter, the reaction mixture was diluted with 100 g of water and the benzene layer was separated, washed with dilute hydrochloric acid and water and dried over anhydrous magnesium sulfate. The low-boiling fraction was then distilled off under reduced pressure to recover an oil. This oily product was purified by preparative liquid chromatography [column: Water's Associates' Prep LC/System 500, Prep

PAK ® 500/SILICA; solvent system: diethyl ether:n-hexane=2:98]. The above procedure yielded 20.2 g of 3-(4-chlorophenoxy)- $\alpha$ -ethynylbenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (yield 90%). The separation of cis- and trans-isomers from each other can be effected by the above-mentioned preparative liquid chromatography. The NMR spectra of such isomers are indicated below.

NMR spectra (90 MHz)  $\delta_{HMS}^{CDCl_3}$ :

cis-Compound: 1.13, 1.16, 1.20, 1.23(each s)6H; 1.72-2.10(m)2H; 2.53-2.60(m)1H; 6.16(d), 6.18(d)1H; 6.32-6.40(m)1H; 6.75-7.43(m)8H

trans-Compound: 1.08, 1.13, 1.17, 1.25(each s)6H; 1.56(d), 1.58(d)1H; 2.04-2.31(m)1H; 2.52-2.61(m)1H; 5.55(d)1H; 6.36-6.43(m)1H; 6.76-7.43(m)8H

## EXAMPLE OF SYNTHESIS-3

The procedure followed in Example of Synthesis-2 was repeated except that 11.7 g of 3-(4-chlorophenoxy)benzyl alcohol was used in lieu of 12.9 g. of 3-(4-chlorophenoxy)- $\alpha$ -ethynylbenzyl alcohol. The resultant oily product was purified by preparative liquid chromatography to obtain 19.6 g of 3-(4-chlorophenoxy)benzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (yield 92%). The NMR spectra of the cis- and trans-isomers obtained by preparative liquid chromatography are in agreement with the spectra of the compounds according to Example of Synthesis-1.

## TEST EXAMPLE-1

Mortality test with houseflies (*Musca domestica*) by topical application method

Each of the compounds according to this invention and the control compounds (Table 2) was accurately weighed and a 0.1% solution of each sample in acetone was prepared. Female adult houseflies (*Musca domestica*) resistant to organophosphorus pesticides, were anesthetized with ether and 0.5  $\mu$ l or 1.0  $\mu$ l of the above solution was micropipetted onto the prothoracic dorsal region of each insect. The insects were then put in a high-walled dish together with feed and the dish was covered with a wire-mesh cover and kept at a temperature of 25° C. The test insects were used in groups of 30 individuals each. After 24 hours the insects were examined for deaths and the percent mortality was calculated. The results are set forth in Table 2.

TABLE 2

Test compound	% Mortality	
	0.5 $\mu$ g/Female	1.0 $\mu$ g/Female
Compound (1)		
cis-	100	100
trans-	100	100
cis-/trans- = 50:50	100	100
Compound (2)		
cis-	100	100
trans-	100	100
cis-/trans- = 50:50	100	100
Compound (A)	"	97
Compound (B)	"	100
Compound (C)	"	100
Compound (D)	"	100
Compound (E)	—	100
Compound (F)	cis-/trans- = 50:50	100
Compound (G)	"	100
Compound (H)	"	100
		60
		93

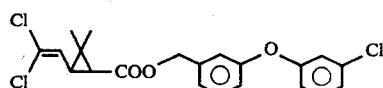
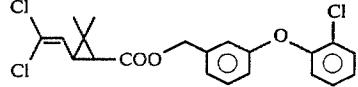
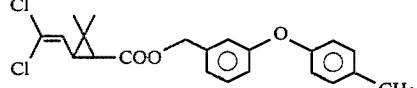
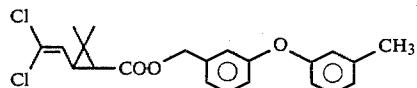
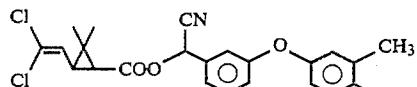
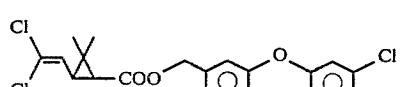
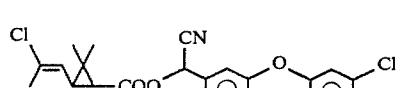


TABLE 2-continued

Test compound	% Mortality	
	0.5 $\mu\text{g}/\text{Female}$	1.0 $\mu\text{g}/\text{Female}$
	"	30 60
	"	80 100
	"	50 80
	"	40 80
	"	0 20
	"	0 27

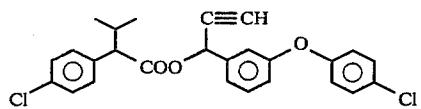
## TEST EXAMPLE-2

Mortality test with green rice leafhoppers (*Nephotettix cincticeps Uhler*) by topical application method

Each of the compounds according to this invention and the control compounds (Table 3) was accurately weighed and dissolved in acetone to prepare a solution

above solution was micropipetted onto the thoracic abdominal region of each insect. Then, the insects were kept at 25° C. with access to rice plant seedlings. The insects were used in groups of 15 individuals each. After 24 hours, the insects were examined for deaths and the percent mortality was calculated. The results are shown in Table 3.

TABLE 3

Test compound	% Mortality		
	0.01 $\mu\text{g}/\text{Female}$	0.1 $\mu\text{g}/\text{Female}$	1.0 $\mu\text{g}/\text{Female}$
Compound (1)	trans-	100	100
	cis-/trans- = 50:50	100	100
Compound (2)	cis-	100	100
	trans-	100	100
	cis-/trans- = 50:50	100	100
Compound (A)	"	80	100
Compound (B)	"	80	100
Compound (C)	"	100	100
Compound (D)	"	100	100
Compound (E)	—	100	100
Compound (F)	cis-/trans- = 50:50	100	100
Compound (G)	"	100	100
Compound (H)	"	100	100
		33	100
			
[hereinafter referred to as Compound (K)]			

of predetermined concentration. Female adult green 65 rice leafhoppers (*Nephotettix cincticeps Uhler*) resistant to organophosphorus and carbamate pesticides were anesthetized with carbon dioxide gas and 0.5  $\mu\text{l}$  of the

Furthermore, there was determined by the above method the median lethal dose [LD<sub>50</sub>: the amount of each test compound which killed 50% of dosed green

TABLE 7-continued

Test compound	Percent decrease of population (%)
trans-	100
cis-/trans- = 50:50	100
Compound (B) cis-/trans- = 50:50	100

## TEST EXAMPLE-6

Fish toxicity test with killifish (*Orizias latipes*)

An acetone solution of one of the test compounds as mentioned in Table 8 was prepared by adding said test compound to 15 ml of acetone. To 10 liters of water was added a predetermined amount of the above acetone solution and the mixture was stirred thoroughly to prepare an aqueous solution containing the test compound in a predetermined concentration. This was used as a test water. After the each test water was moderately aerated, ten killifishes (*Orizias latipes*) with a body weight of about 0.25 g and a body length of about 2.5 cm were released into said each test water which was maintained at  $25 \pm 1^\circ \text{C}$ . After 48 hours, the test fish was examined for death. The TLm (median tolerance limit, ppm) was determined. The results are set forth in Table 8.

TABLE 8

Test compound	TLm (48 hrs.)	
	ppm	
Compound (1)	cis-	>10
	trans-	>10
	cis-/trans- = 50:50	>10
Compound (2)	cis-	>10
	trans-	>10
	cis-/trans- = 50:50	>10
Compound (B)	"	0.040
Compound (C)	"	0.026
Compound (G)	"	0.15

## TEST EXAMPLE-7

Fish toxicity test with guppies (*Lebistes reticulatus*)

To 5 liters of water were added 250 mg of Sorpol SM-200 (trademark, Toho Chemical Co., Ltd.) as a surfactant and 2.5 ml of an acetone solution containing one of the test compounds in a predetermined concentration. The mixture was stirred thoroughly to prepare a test water. Ten female guppies (*Lebistes reticulatus*) of from 3 to 4 months of age were released into the test water which was maintained at  $20^\circ \text{C}$ . and the TLm (median tolerance limit, ppm) was determined. The results are set forth in Table 9.

TABLE 9

Test compound	TLm (48 hrs.)	
	ppm	
Compound (1) cis-/trans- = 50:50	>5	
Compound (2) "	>10	
Compound (B) "	<0.5	
Compound (C) "	<0.5	
Compound (D) "	<0.5	
Compound (E) —	<0.5	
Compound (F) cis-/trans- = 50:50	<0.5	
Compound (G) "	<1.0	

## TEST EXAMPLE-8

Fish toxicity test with carp (*Cyprinus carpio L*)

An acetone solution of one of the test compounds as mentioned in Table 10 and Tween-20 (the same surfac-

tant as mentioned hereinbefore) was prepared. To 50 liters of water (30 cm deep) in a glass tank was added the above acetone solution. The mixture was stirred thoroughly to prepare an aqueous solution containing the test compound in a predetermined concentration. This was used as a test water. Five carps (*Cyprinus carpio L*) with a body weight of about 6 g and a body length of about 6 cm were released into each test water which was maintained at  $21 \pm 1^\circ \text{C}$ . After 48 hours, the test fish was examined for death. The TLm (median tolerance limit, ppm) was determined. The test water was moderately aerated. The results are set forth in Table 10.

Toxicity test with water-fleas (*Daphnia pulex*)

An acetone solution of one of the test compounds as mentioned in Table 10 and Tween-20 (the same surfactant as mentioned hereinbefore) was prepared. To 100 ml of water in a high-walled dish (9 cm in diameter, 7 cm deep) was added the above acetone solution. The mixture was stirred thoroughly to prepare an aqueous solution containing the test compound in a predetermined concentration. This was used as a test water. Twenty water-fleas (*Daphnia pulex*) were released into each test water which was maintained at  $25 \pm 1^\circ \text{C}$ . After 6 hours, the water-fleas were examined for deaths. The TLm (median tolerance limit, ppm) was determined. The results are set forth in Table 10.

TABLE 10

Test compound	TLm, ppm		
	Carp (48 hrs.)	Water-flea (6 hrs.)	Ranking
Compound (1) cis-/trans- = 20:80	2.6	>40	B
trans-	4.5	>40	B
Compound (2) cis-	0.83	>40	B
cis-/trans- = 50:50	2.8	>40	B
cis-/trans- = 30:70	4.9	>40	B
cis-/trans- = 10:90	7.2	>40	B
trans-	>10	>40	A
Compound (B) cis-/trans- = 50:50	0.015	—	C
Compound (C) "	0.0045	—	C
Compound (D) "	0.0051	—	C
Compound (E) —	0.0032	—	C
Compound (G) cis-	0.013	5.0	C
cis-/trans- = 50:50	0.040	—	C
trans-	0.090	1.7	C
Compound (H) cis-/trans- = 50:50	0.063	—	C
Compound (I) —	0.032	—	C

The above ranking with symbols A, B and C were determined according to Japanese regulations relative to application of agricultural chemicals, and these symbols are defined as follows:

A: TLm (48 hrs.) value  $>10$  ppm for carp and TLm (3 hrs.) value  $>0.5$  ppm for water flea, wherein toxicity to fishes is not observed by usual application.

B: TLm (48 hrs.) value 10-0.5 ppm for carp; or TLm (48 hrs.) value  $>10$  ppm for carp and TLm (3 hrs.) value  $<0.5$  ppm for water flea, wherein appreciable toxicity to fishes is not observed by usual application but may be observed when applied to wide area at one time.

C: TLm (48 hrs.) value  $<0.5$  ppm for carp, wherein toxicity to fishes is so strongly observed by usual application that both the application method and application area are strictly restricted.

rice leafhoppers ( $\mu\text{g/g}$ ) of the compounds (1) and (2) according to this invention, the control compounds (A) and (B), carbamate pesticide, i.e. carbaryl and Bassa (o-sec-butylphenyl methylcarbamate), and organophosphorus pesticide, i.e. fenitrothion, diazinon and malathion. The results are set forth in Table 4.

TABLE 4

Test compound	LD <sub>50</sub> , $\mu\text{g/g}$
Compound (1)	cis-/trans- = 50:50
	cis-/trans- = 30:70
	trans-
Compound (2)	cis-
	cis-/trans- = 50:50
	cis-/trans- = 30:70
Compound (A)	trans-
	cis-/trans- = 50:50
	cis-/trans- = 50:50
Compound (B)	29.5
Carbaryl	93.8
Bassa	4050
Fenitrothion	72.2
Diazinon	565
Malathion	

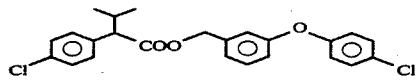
## TEST EXAMPLE-3

Mortality test with rice stem borers (*Chilo suppressalis Walker*) by topical application method

Each of the compounds according to this invention and the control compounds (Table 5) was accurately weighed and dissolved in acetone to prepare a solution of predetermined concentration. Using a microsyringe, 0.5  $\mu\text{l}$  of the above solution was applied to the thoracic abdominal region of each final-instar larva of rice stem borer (*Chilo suppressalis Walker*). Thereafter, the test larvae were released on a filter paper imbibed with water in a dish 9 cm in diameter and kept at a temperature of 25° C. The test larvae were used in groups of 20 individuals each. After 24 hours the larvae were examined for deaths and the percent mortality was calculated. The results are tabulated in Table 5.

TABLE 5

Test compound	% Mortality	
	1.0 $\mu\text{g}/\text{Larva}$	10 $\mu\text{g}/\text{Larva}$
Compound (1)	100	100
cis-	85	100
trans-	100	100
cis-/trans- = 50:50	100	100
Compound (2)	100	100
cis-	100	100
trans-	100	100
cis-/trans- = 50:50	100	100
Compound (A)	45	100
Compound (B)	95	100
Compound (C)	95	100
Compound (D)	100	100
Compound (E)	—	100
Compound (G)	40	100
cis-	85	100
trans-	90	100
cis-/trans- = 50:50	90	100
Compound (H)	15	90



[hereinafter referred to as Compound (J)]

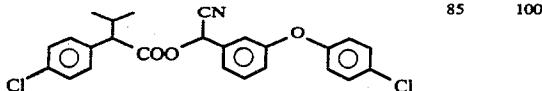


TABLE 5-continued

Test compound	% Mortality	
	1.0 $\mu\text{g}/\text{Larva}$	10 $\mu\text{g}/\text{Larva}$
[hereinafter referred to as Compound (L)]		

## TEST EXAMPLE-4

10 Mortality test with tobacco cutworms (*Prodenia litura Fabricius*) by topical application method

15 Each of the compounds according to this invention and the control compounds (Table 6) was accurately weighed and dissolved in acetone to prepare a solution of predetermined concentration. Using a microsyringe, 0.5  $\mu\text{l}$  of the above solution was dripped onto the thoracic abdominal region of each of 3-instar tobacco cutworm (*Prodenia litura Fabricius*) larvae. Thereafter, the larvae were released together with feed on a filter paper in a dish 9 cm in diameter and kept at a temperature of 25° C. The test larvae were used in groups of 20 individuals each. After 24 hours the insects were examined for 20 deaths and the percent mortality was calculated. The results are shown in Table 6.

TABLE 6

Test compound	% Mortality	
	0.1 $\mu\text{g}/\text{Larva}$	1.0 $\mu\text{g}/\text{Larva}$
Compound (1)	100	100
cis-	100	100
trans-	100	100
cis-/trans- = 50:50	100	100
Compound (2)	100	100
cis-	100	100
trans-	100	100
cis-/trans- = 50:50	100	100
Compound (A)	35	—
Compound (B)	85	—
Compound (G)	65	—
Compound (H)	60	—
Compound (I)	0	—
Compound (K)	0	—
Compound (L)	0	—

## TEST EXAMPLE-5

45 Mortality test with two-spotted spider mites (*Tetranychus urticae Koch*) by spray application method

To a 5% aqueous solution of acetone was added dropwise a small amount of Tween-20 (polyethylene sorbitan monolaurate) as a surfactant. Then, each of the 50 compounds according to this invention and the control compounds (Table 7) was accurately weighed and dissolved in the above 5% acetone-water solution to prepare a solution of 200 ppm. From 30 to 50 adult two-spotted spider mites (*Tetranychus urticae Koch*) were released on the leaves of kidney-bean plants in the dicotyledonous stage in a pot 9 cm in diameter, followed by 55 a spray application of the above solution. The pot was kept in a constant-temperature chamber at 26° C. and two days later the mites were examined for deaths. The percent decrease of population was then calculated. 60 The test compounds and results are shown in Table 7.

TABLE 7

Test compound	Percent decrease of population (%)	
	1.0 $\mu\text{g}/\text{Larva}$	10 $\mu\text{g}/\text{Larva}$
Compound (1)	100	100
cis-	100	100
trans-	100	100
cis-/trans- = 50:50	100	100
Compound (2)	100	100

## TEST EXAMPLE-9

## Acute toxicity test in rat by the oral route

Male rat weighting 260 to 270 g were orally dosed with each test compound as dissolved in olive oil (0.5 ml/100 g body weight) and the median lethal dose [LD<sub>50</sub>: the amount of each test compound which killed 50% of dosed rats (mg/kg)] after 7 days was determined. The results are set forth in Table 11.

TABLE 11

Test compound	cis-/trans- = 50:50	LD <sub>50</sub> mg/kg
Compound (1)	cis-/trans- = 50:50	>3000
Compound (2)	"	>3000
Compound (B)	"	300
Compound (C)	"	310
Compound (E)	—	440

## FORMULATION EXAMPLE-1

Thirty (30) parts each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) were prepared. To each of them were added 50 parts of xylol and 20 parts of Sorpol SM-200 (the same surfactant as mentioned hereinbefore). Each mixture was stirred well to prepare 30% emulsifiable concentrates of the respective active compounds.

## FORMULATION EXAMPLE-2

One (1) part each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) was prepared. To each of them were added 3 parts of dimethylformamide and 1 part of Tween-20 (the same surfactant as mentioned hereinbefore) followed by thorough mixing. Each mixture was diluted with water with stirring to make 100 parts of a 1% emulsifiable concentrate of the corresponding compound.

## FORMULATION EXAMPLE-3

Two-tenths (0.2) parts each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) were respectively dissolved in 20 parts of acetone, followed by addition of 99.8 parts of clay. After thorough stirring, the acetone was evaporated from each mixture and the residue was further stirred well in a triturator to prepare a 0.2% dust of the corresponding compound.

## FORMULATION EXAMPLE-4

Five-tenths (0.5) parts each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) were respectively dissolved in 20 parts of acetone, followed by addition of 99.5 parts of clay. After thorough stirring, the acetone was evaporated from each mixture and the residue was further stirred well in a triturator to prepare a 0.5% dust of the corresponding compound.

## FORMULATION EXAMPLE-5

Two-tenths (0.2) parts each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) was dissolved in kerosene with stirring to make 100 parts. The above procedure yielded oil preparations of the respective active compounds.

To 20 parts each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) was added 5 parts of Sorpol SM-200 (the same surfactant as mentioned hereinbefore). After thorough mixing, 75 parts of clay was added to each mixture and stirred well in a triturator. The above procedure yielded wettable powders of the respective active compounds.

## UTILITY EXAMPLE-1

A 1% emulsifiable concentrate of each test compound as prepared by the procedure described in Formulation Example 2 was diluted with water to prepare a test solution of predetermined concentration.

Rice plants, 4 weeks after sowing (cultivated in a pot 6 cm in diameter, 7 seedlings) were dipped in the above solution and after allowing them to dry in the air, the pot was covered with a wire-mesh cage. Then, 30 adult brown planthoppers (*Nilaparvata lugens Stal*) were released into the cage and the pot was kept in a constant-temperature chamber at 25° C. After 24 hours the insects were examined for deaths and the median lethal concentration [LC<sub>50</sub>; the concentration (ppm) of each test compound which kills 50% of the test insects in 24 hours] was determined. The results are set forth in Table 12.

To further confirm the low toxicity to fish and high pesticidal activity of Compounds (1) and (2) according to this invention as evidenced by the fish toxicity tests with carps and the above tests, fish toxicity safety factors were calculated from the fish toxicity and pesticidal test data. These fish toxicity safety factors are indicators of safety to fish inhabiting a paddy field to which Compounds (1) and (2) may be actually applied for pest control purposes.

It is first assumed that such a pesticidal solution would normally be applied at the rate of 100 l per 10 acres of paddy field. It is also assumed that a solution (100 l) corresponding to the LC<sub>50</sub> of the compounds would be applied to 10 acres of a paddy field carrying a cover water with a depth of 5 cm above ground surface and that all the solution would then find its way into the cover water. The expected maximum concentration of the compound in the cover water is then calculated. The fish toxicity safety factor of a pesticidal compound is defined as the value obtained by dividing the TL<sub>m</sub> (ppm) of the particular compound by the maximum concentration of the compound in cover water. The meaning of the value of the fish toxicity safety factor being one (1) is that the maximum concentration of the particular compound in cover water corresponds to the TL<sub>m</sub> of said compound. It is understood that when the pesticidal compound having a fish toxicity safety factor value of less than one (1) is applied to a paddy field, it has a risk of destroying the fish inhabiting there, and that the higher the safety factor value, the higher is the safety of the compound to fish.

This fish toxicity safety factor will now be explained in further detailed by taking the trans-isomer of Compound (2) of this invention as an example.

The quantity of water required to form a 5 cm-deep cover water over 10 acres of paddy field is 50 tons and if 100 liters of a solution corresponding to the LC<sub>50</sub> of the trans-isomer of Compound (2) is applied to the above cover water, the maximum concentration of the trans-isomer in the water will be 0.36 ppm. On the other hand,

the toxicity to fish of this compound is TLm > 10 ppm. Therefore, by dividing the TLm (i.e. > 10 ppm) by the above cover water maximum concentration (i.e. 0.36 ppm), we obtain a fish toxicity safety factor of > 28. Thus, the concentration of the trans-isomer of Compound (2) which kills 50% of pests corresponds to less than 1/28 of the concentration of the same isomer which kills 50% of fish. In other words, this means that the trans-isomer of Compound (2) is extremely safe to fish.

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TABLE 12

Test compound	Toxicity to fish TLm (ppm)	Pesticidal activity LC <sub>50</sub> (ppm)	Fish toxicity safety factor
Compound (1)	cis-/trans- = 20:80	2.6	520
	trans-	4.5	650
Compound (2)	cis-	0.83	200
	cis-/trans- = 50:50	2.8	190
	cis-/trans- = 30:70	4.9	180
	cis-/trans- = 10:90	7.2	180
	trans-	>10	180
Compound (B)	cis-/trans- = 50:50	0.015	700
Compound (C)	"	0.0045	210
Compound (G)	cis-	0.013	620
	cis-/trans- = 50:50	0.04	450
	trans-	0.09	380
Compound (E)	—	0.0032	1550
Compound (L)	—	0.032	2260
			0.0071

## UTILITY EXAMPLE-2

A 30% emulsifiable concentrate of each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and Compound (2) as prepared by the procedure described in Formulation Example-1 was diluted with water to a concentration of 80 ppm as active compound. Rice plants 4 weeks after sowing in pots (each pot 6 cm in diameter, 7 seedlings) were sprayed with the above solution at the rate of 7 ml/pot and, after drying in the air, each pot was covered with a wire-mesh cage. Then, 20 female adult green rice leafhoppers (*Nephrotettix cincticeps Uhler*) were released into the cage. The caged pots were kept in a constant-temperature chamber at 25° C. After 24 hours, the test insects were examined for deaths and the percent mortality was determined. In all groups, the mortality values were not less than 90%.

45

## UTILITY EXAMPLE-3

A 30% emulsifiable concentrate of each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) as prepared by the procedure described in Formulation Example-1 was diluted with water to a concentration of 80 ppm as active compound. Rice plants 4 weeks after sowing in pots (each pot 6 cm in diameter, 7 seedlings) were sprayed with the above diluted solution at the rate of 7 ml/pot and, after drying in the air, each pot was covered with a wire-mesh cage. Then, 30 adult small brown planthoppers (*Laodelphax striatellus Fallén*) were released into the cage. The pots were kept in a constant-temperature chamber at 25° C. After 24 hours the test insects were examined for deaths and the percent mortality was calculated. In all groups, the mortality was not less than 90%.

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## UTILITY EXAMPLE-4

A 0.2% dust preparation of each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers

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of Compound (1) and of Compound (2) as prepared by the procedure described in Formulation Example-3 was applied to rice seedlings by means of a bell-jar duster at the rate of 5 kg per 10 acres. Then, 30 green rice leafhoppers (*Nephrotettix cincticeps Uhler*) resistant to organophosphorus and carbamate pesticides were released. After 24 hours the insects in each group were examined for deaths and the percent mortality was calculated. In all cases, the mortality was not less than 90%.

## UTILITY EXAMPLE-5

An acetone solution of one of the test compounds as mentioned in Table 13 and Tween-20 (the same surfactant as mentioned hereinbefore) was prepared. This acetone solution was diluted with water to prepare a solution containing the test compound in a predetermined concentration. Leaves of soy bean in pots were sprayed with the above diluted solution at the rate of 20 ml/pot and, after one day, ten 3-instar larvae of tobacco cutworm (*Prodenia litura*) were released on the leaves. The pots were kept in a constant-temperature chamber at 25° C. After 2 days, the test larvae were examined for deaths and the percent mortality was calculated. The results are set forth in Table 13.

TABLE 13

Test compound	% Mortality	
	6.5 ppm	13 ppm
Compound (1) cis-/trans- = 50:50	90	100
Compound (2) "	100	100
Compound (B) "	60	90
Compound (H) "	40	100
	10	100
	0	90

## UTILITY EXAMPLE-6

A 0.5% dust preparation of each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) as prepared by the procedure described in Formulation Example-4 was applied to rice seedlings by means of a bell-jar duster at the rate of 1 kg per 10 acres. Then, 30 green rice leafhoppers (*Nephrotettix cincticeps*) resistant to organophosphorus and carbamate pesticides were released. After 24 hours, the insects in each group were examined for deaths and the percent mortality was calculated. In all cases, the mortality was not less than 90%.

## UTILITY EXAMPLE-7

A 0.5% dust preparation of each of the cis- and trans-isomers and a 50:50 mixture of the cis- and trans-isomers of Compound (1) and of Compound (2) as prepared by the procedure described in Formulation Example-4 was applied to rice seedlings, on which 30 adult brown planthoppers (*Nilaparvata lugens*) were released, by means of a bell-jar duster at the rate of 1 kg per 10 acres. After 24 hours, the insects in each group were examined for

deaths and the percent mortality was calculated. In all cases, the mortality was not less than 90%.

## UTILITY EXAMPLE-8

## Phytotoxicity test

A 2,000 ppm solution of each of the cis- and trans-isomers and a 50:50 mixture of cis- and trans-isomers of Compound (1) and of Compound (2), and a 50:50 mixture of the cis- and trans-isomers of Compound (B) and Compound (E) was applied to the leaves of the following crop plants.

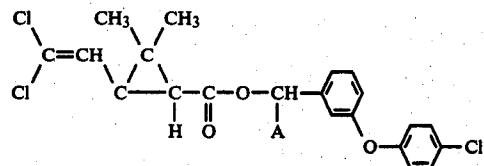
Test crop plant:

Name	Leaf stage	15
Chinese cabbage	4th-5th leaf stage	
Radish	2nd-3rd leaf stage	
Tomato	3.5th-4.5th leaf stage	
Cucumber	2nd-2.5nd leaf stage	
Eggplant	2.5nd-3.5th leaf stage	
Beat	2nd-3rd leaf stage	
Soy bean	1st dicotyledonous stage	

After 10 days, the crop plants were examined for their phytotoxicities. Compounds (1), (2) and (B) each did not cause any injury to each one of the crop plants. But, Compound (E) caused chlorosis to each one of the crop plants and did large damage to the same.

What is claimed as new and intended to be covered by Letters Patent of the United States is:

1. A method for controlling insects or acarids which comprises applying to a habitat of the insects or acarids an effective amount of a substituted cyclopropanecarboxylic acid ester of the general formula:



20 wherein A is a hydrogen atom or an ethynyl group and said ester is applied to rice paddy.

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